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DETECTION OF HYDROGEN CYANIDE. A TEST READILY ADAPTABLE FOR THE XM256 CHEMICAL AGENT DETECTOR KIT

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Edgewood Arsenal
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(U) A successful test for hydrogen cyanide was developed for the XM256 chemical agent detector kit. Prior to the detection, papers impregnated with cupric acetate were spotted with a solution of p,p'-tetramethyldiaminodiphenylmethane (tetrabase) in methyl alcohol. The immediate appearance of a deep blue coloration against a very light blue background indicated the presence of hydrogen cyanide. The cupric acetate papers and tetrabase-methyl alcohol solution passed the heat stability requirement (65°C for 30 days).

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Task 1W663721D60108

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FOREWORD

The work described in this report was performed under Task 1W663721D60108, Chemical Agent Detector Kits. The experimental data are contained in notebook 8731. The work was begun on 30 May and completed on 30 June 1972.

DIGEST

A successful test for hydrogen cyanide was developed for the XM256 chemical agent detector kit. Prior to the detection, papers impregnated with cupric acetate were spotted with a solution of p,p'-tetramethyldiaminodiphenylmethane (tetrabase) in methyl alcohol. The immediate appearance of a deep blue coloration against a very light blue background indicated the presence of hydrogen cyanide. The cupric acetate papers and tetrabase-methyl alcohol solution passed the heat stability requirement (65°C for 30 days).

CONTENTS

DETECTION OF HYDROGEN CYANIDE. A TEST READILY ADAPTABLE FOR THE XM256 CHEMICAL AGENT DETECTOR KIT

I. INTRODUCTION.

A. Administrative.

Directorate of Defense and Engineering (DDE) is charged with the responsibility of developing a chemical agent detector kit. One of the problems encountered with the kit is the development of a test for hydrogen cyanide. DDE requested Chemical Laboratory to develop a reliable, sensitive test for hydrogen cyanide.

B. Technical.

Three main tests have been used in the past in various detector kits for the detection of hydrogen cyanide.[1] These tests are (1) induced oxidation of amines, (2) liberation of acid from mercuric chloride, and (3) formation of cyanogen chloride. Only the induced oxidation of amines (tetrabase) was investigated in this study for application to the chemical detector kit.

In this test, hydrogen cyanide reacts with cupric acetate forming cuprous cyanide and nascent cyanogen as shown in equation 1.[1-5]

$$2HCN + Cu(OCOCH_3)_2 \longrightarrow Cu(CN)_2 + 2HOCOCH_3 \quad (1)$$
$$\downarrow$$
$$\tfrac{1}{2}Cu_2(CN)_2 + \tfrac{1}{2}(CN)_2$$

Nascent cyanogen then oxidizes tetrabase to a deep blue compound as shown in equation 2.

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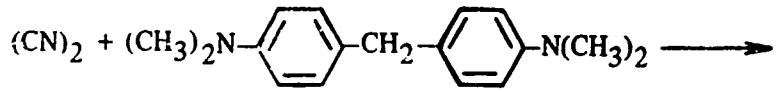
[1] Falkof, Melvin M., and Gehauf, Bernard. History of Research and Development of the Chemical Warfare Service in World War II. Volume 11, Detectors and Alarms. 2 October 1951. UNCLASSIFIED Report.

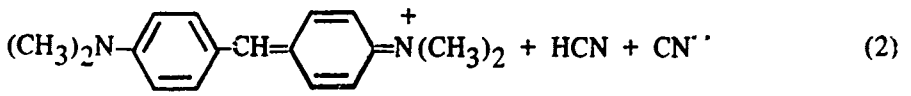
[2] Falkof, Melvin M., Gehauf, Bernard, and Witten, Benjamin. TDMR 1005. Kit, Chemical Agent Analyser, E10. 29 March 1945. UNCLASSIFIED Memorandum Report.

[3] Gehauf, Bernard, and Falkof, Melvin M. TDMR 507. Chemical Agent Detectors, Gas Absorption Type. 30 December 1942. UNCLASSIFIED Memorandum Report.

[4] Wilson, C. L., and Wilson, D. W. Comprehensive Analytical Chemistry. I^A, Classical Analysis. Elsevier Publishing Company, New York, New York. 1959.

[5] Forsman, Nils, et al. C-stridsmedlen egenskaper och skydd, Supplement Till "FOA Orienterar OM BC-Stridsmedel" 2, 39 (1972).





(2)

In practice, Whatman chromatographic papers were dipped into the appropriate cupric solution, allowed to dry overnight, moistened with tetrabase solution, and observed. Exposure to hydrogen cyanide (holding the test paper over an opened bottle of sodium cyanide was sufficient) promptly produced an intense blue coloration. Interference to the test consists of slow air oxidation to give a blue coloration that is light at first but darkens on standing in air. Oxidation by such chemicals as chlorine and bromine gives an immediate blue color.[4]

The best cupric papers were prepared by dipping Whatman 3MM chromatographic paper (preferred over Whatman No. 31 extra-thick chromatographic paper) in a solution of 10 gm of cupric acetate in 400 ml of water. All cupric acetate papers were stable in an oven heated to 65° for 30 days, whereas cupric sulfate papers deteriorated (turned brown) within a week. The addition of glycerin or ethylene glycol to the formulation failed to prevent the deterioration of the cupric sulfate papers.

Oven stability and detection tests of the tetrabase solutions proved methyl alcohol to be superior to benzene or acetone. A solution of 0.25 gm of tetrabase in 100 ml of methyl alcohol was sufficient to produce a positive hydrogen cyanide test.

The selection of cupric acetate papers and tetrabase-methyl alcohol solution for the hydrogen cyanide test gave another unexpected advantage. Cupric sulfate papers moistened with tetrabase-methyl alcohol solution gave an initial small amount of yellow coloration which was not present when cupric acetate papers were employed. The nature of the yellow coloration was not investigated.

A variation in the procedure was introduced in which the detection of hydrogen cyanide, indicated by a deep blue coloration, appeared in the form of the letters "HCN" rather than the usual round spot. However, since impregnated cupric acetate papers have a light blue coloration, it was necessary to mask the coloration with malachite green, a triphenylmethane dye. Thus, Whatman 3MM chromatographic paper was dipped into a dilute solution of aqueous malachite green and dried (light greenish tint).

The dried malachite green papers were marked with a hand stamp containing the letters "HCN" (3/16 inch in height) wetted with cupric acetate solution. Drying gave a homogeneous paper with a light greenish tint. The addition of tetrabase-methyl alcohol solution to the hand-stamped area and exposure to hydrogen cyanide produced an immediate dark blue coloration of the letters "HCN."

II. EXPERIMENTAL.

A. Chemicals.

1. Cupric Salt:

Cupric acetate

Cupric chloride

Cupric sulfate

Solvents.

Water

Ethylene glycol

Glycerin

2. Triphenylmethane Dye.

Malachite green (a hydrochloride)*

3. Whatman Chromatographic Paper.

No. 31 extra thick

3MM (5 cm wide)

4. Oxidizable Amine.

p,p'-Tetramethyldiaminodiphenylmethane (tetrabase)**

Solvents.

Acetone

Benzene

Methyl alcohol

5. Source of Hydrogen Cyanide.

Sodium cyanide

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* Industrial Chemicals Division, Allied Chemical Corporation.

** Fisher Scientific Company.

B. General Procedure.

1. The Cupric Test Papers.

a. Cupric Sulfate.

Large sheets of Whatman No. 31 extra-thick chromatographic paper (22½ by 18 inches) were cut in 3-inch widths; from Whatman 3MM chromatographic paper (5-cm-width roll) 18-inch lengths were cut. The appropriate solution was transferred to a dipping tank 8 inches long by 3½ inches wide by 8½-inches deep and, while holding both ends of the respective paper strip, swished back and forth in the solution until fully saturated, removed, and hung by a paper clip on a line to dry. Corrosion was prevented by the insertion of polyethylene film between the paper clip and wet paper strip. The papers were allowed to dry overnight at room temperature.

A threefold scale-up of the following solutions were prepared for the dip tank:

10 gm of cupric sulfate/100 ml of water

10 gm of cupric sulfate/10 ml of glycerine/90 ml of water

10 gm of cupric sulfate/10 ml of ethylene glycol/90 ml of water

b. Cupric Chloride.

A few small pieces of Whatman No. 31 extra-thick chromatographic paper were saturated with the following solutions:

1 gm of $CuCl_2 \cdot 2H_2O$/1 ml of ethylene glycol/9 ml of water

0.5 gm of $CuCl_2 \cdot 2H_2O$/1 ml of ethylene glycol/9 ml of water

c. Cupric Acetate.

Cupric acetate (not very soluble in water) papers were prepared according to the procedure in 1a above. Concentrations of the solutions were as follows:

10 gm of $Cu(OCOCH_3)_2 \cdot H_2O$/400 ml of water

10 gm of $Cu(OCOCH_3)_2 \cdot H_2O$/300 ml of water

1.5 gm of $Cu(OCOCH_3)_2 \cdot H_2O$/300 ml of water

d. Cupric Acetate. Malachite green.

Three 18-inch-long sheets of 3MM Whatman chromatographic paper (5 cm wide) were dipped into a filtered solution of 0.4 gm of malachite green in 750 ml of water (very poor solubility), allowed to dry overnight, and cut into 3/4 by 2-inch strips. The tinted papers were marked with the letters "HCN" by means of a rubber stamp and wetted with a solution of 10 gm of cupric acetate in 400 ml of water.

2. The Tetrabase Solutions.

a. Acetone.

A solution of 5 gm of tetrabase in 100 ml of acetone (very light pink color) was prepared. Two 25-ml portions were transferred to two pyrex mailing tubes of 50-ml capacity, sealed, and placed in an oven heated at 65°C for 2 weeks.

b. Benzene.

The procedure of 2a was repeated with benzene as the solvent (5 gm of tetrabase/100 ml of benzene - a light yellow solution).

c. Methyl Alcohol.

The procedure of 2a was repeated with methyl alcohol as the solvent. Due to poor solubility, the composition of the solution was only 1 gm of tetrabase/100 ml of methyl alcohol. This solution was slightly darker than the benzene solution of 2b.

III. RESULTS.

A. Stability Tests.

1. Cupric Test Papers.

Cupric test papers prepared according to the general procedure, section IIB, were placed in an oven heated to 65°C. Most cupric sulfate papers deteriorated within 1 to 2 weeks. Papers prepared from cupric chloride were medium to very dark green and were consequently disregarded. No change was observed in the cupric acetate papers which remained a very light blue after 30 days at 65°C.

2. Tetrabase Solutions.

The acetone-tetrabase solution changed from very light pink to medium red within a few days after heating in a sealed tube at 65°C. Little or no change was observed after that time. The benzene-tetrabase solution remained light yellow and the methyl alcohol-tetrabase solution was only slightly darker after heating in sealed tubes for 2 weeks at 65°C.

B. Sensitivity Tests.

Stability tests indicated that the best hydrogen cyanide detector system would be composed of cupric acetate papers and tetrabase solutions of methyl alcohol or benzene. Failure to give a favorable hydrogen cyanide test eliminated the latter solvent from further consideration. Hydrogen cyanide was successfully detected when the concentration of tetrabase in methyl alcohol was decreased from 1 gm to 0.25 gm/100 ml.

The moistening of cupric acetate papers (prepared from 0.5 gm of copper acetate and 100 ml of water) with tetrabase-methyl alcohol solution gave an almost immediate light greenish-blue coloration. Increasing the amount of cupric acetate in the paper successfully masked the color. Thus, papers prepared from a solution of 10 gm of cupric acetate in 400 ml of water and moistened with a drop of a solution of 0.25 gm of tetrabase in 100 ml of methyl alcohol gave a negligible color change after exposure to the air for as long as 90 minutes but gave an immediate dark blue coloration when exposed to hydrogen cyanide. Holding the test paper over an opened bottle of sodium cyanide was sufficient to give a positive test for hydrogen cyanide.

An initial, temporary small amount of yellow coloration was observed when tetrabase-methyl alcohol solution was added to cupric sulfate papers. The yellow coloration was not present when cupric acetate papers were used. The nature of the yellow coloration was not further investigated.

The dry malachite green tinted papers were observed to have only a faint greenish-blue cast. When the "HCN" impression of the cupric acetate solution was made on the paper, by means of the hand stamp, the lettering was visible but it slowly disappeared as drying progressed. When a drop of a solution of 0.25 gm of tetrabase in 100 ml of methyl alcohol was added, no signs were visible. However, exposure to an open bottle of sodium cyanide produced an immediate dark blue coloration of the letters "HCN."

IV. DISCUSSION.

One of the reliable methods for the detection of hydrogen cyanide, and the subject of this study, depends upon the liberation of nascent cyanogen when hydrogen cyanide reacts with cupric salts. The nascent cyanogen then reacts with certain amines, such as tetrabase, to yield deep blue colored compounds In practice, test papers prepared from a cupric salt are moistened with a solution of tetrabase, and exposure to hydrogen cyanide produces a deep blue coloration.

The reagents utilized in the detection of hydrogen cyanide were required to be stable at 65°C for 30 days. This criterion eliminated the use of cupric sulfate papers which deteriorated and tetrabase-acetone solution which darkened upon heating and consequently gave unsatisfactory results. Tetrabase-benzene solution was eliminated from consideration, since it failed to give a positive hydrogen cyanide test.

The rigid stability requirements were passed by solution of tetrabase in methyl alcohol and by test papers prepared from aqueous cupric acetate solution. Cupric acetate test papers moistened with tetrabase methyl alcohol solution gave an immediate deep blue coloration when exposed to hydrogen cyanide. Sufficient hydrogen cyanide is present for detection from an opened bottle of sodium cyanide.

V. CONCLUSION.

A reliable test for hydrogen cyanide was developed for the XM256 chemical agent detector kit.

LITERATURE CITED

1. Falkof, Melvin M., and Gehauf, Bernard. History of Research and Development of the Chemical Warfare Service in World War II. Volume 11, Detectors and Alarms. 2 October 1951. UNCLASSIFIED Report.

2. Falkof, Melvin M., Gehauf, Bernard, and Witten, Benjamin. TDMR 1005. Kit. Chemical Agent Analyser, E10. 29 March 1945. UNCLASSIFIED Memorandum Report.

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